National Institute of Standards & Technology

Certificate of Analysis

Standard Reference Material® 2296

Reformulated Gasoline (13 % ETBE)

This Standard Reference Material (SRM) is intended primarily for use in the calibration of instruments and the evaluation of methods used for the determination of total sulfur, benzene, toluene, and ethyl *tert*-butyl ether (ETBE) in reformulated gasoline or similar matrix. A unit of SRM 2296 consists of a set of two 20-mL unscored ampoules (see "Instructions for Use") containing a synthetic gasoline blend of twenty-five organic compounds.

Certified Concentration Values: Certified concentration values expressed as mass fractions and associated 95 % confidence intervals are given in Table 1. The mass fraction (mass constituent/total mass) of sulfur is based on isotope-dilution thermal ionization mass spectrometry [1]. The mass fraction of benzene and the mass fraction of ETBE are based upon split-injection, flame-ionization detection gas chromatographic (GC-FID) analysis coupled with gravimetry. The mass fraction of toluene is based upon reverse-phase liquid chromatography, GC-FID analysis, and gravimetry.

Reference Concentration Values: Reference concentration values expressed as mass fractions and associated 95 % confidence intervals are given in Table 2. The reference value of water is based on coulometric Karl Fischer titration. The major aromatic and olefinic constituents of the synthetic base gasoline were determined using GC-FID after a rigorous evaluation of the purity of the constituent stock materials by gas chromatography-mass spectrometry (GCMS). The reference values of the organic components of this SRM have been deduced from the GC-FID measurements of the base gasoline composition combined with the known mass of the various components of the mixture. The aromatic, olefinic, and saturate composite reference values are the sum of all constituents identified as belonging to each of these groupings. The reference value of the total organic oxygen composite is the sum of the oxygen mass fraction of all identified organic oxygenates.

Statement of Uncertainty: The 95 % confidence interval for each certified and reference value has been assigned on the basis of analytical judgment [2]. It incorporates estimates of analytical precision, known biases among methods of differing analytical reliability, reliability estimates for the mass-spectrometric identification of impurities, and allowance for apparent heterogeneity among the ampoules. The certified mass fraction of each component is expected to lie within the specified interval with a 95 % level of confidence. The reference values do not meet NIST criteria for certification and the uncertainty associated with each reference value may not include all sources of uncertainty.

Expiration of Certification: The certification of SRM 2296 is valid, within the measurement uncertainties specified, until **31 December 2012**, provided that the SRM is handled in accordance with the instructions given in this certificate. However, the certification is invalid if the SRM is damaged, contaminated, or modified.

Maintenance of SRM Certification: NIST will monitor this SRM over the period of its certification. If substantive technical changes occur that affect the certification before the expiration of this certificate, NIST will notify the purchaser. Registration (see attached sheet) will facilitate notification.

The overall direction and coordination of technical measurements leading to the certification were under the chairmanship of G.W. Kramer and F.R. Guenther of the NIST Analytical Chemistry Division.

Stephen A. Wise, Chief
Analytical Chemistry Division

Gaithersburg, MD 20899
Certificate Issue Date: 22 February 2006
See Certification Revision History on Last Page

Robert L. Watters, Jr., Chief
Measurement Services Division

Analytical measurements required for certification of this SRM were performed by S.N. Chesler, S.J. Choquette, F.R. Guenther, T.L. Green, W.R. Kelly, J.L. Mann, S.A.Margolis, L.C. Sander, and R.D. Vocke, Jr. of the NIST Analytical Research Division. Data analysis was performed by D.L. Duewer of the NIST Analytical Chemistry Division.

The support aspects involved in the issuance of this SRM were coordinated through the NIST Measurement Services Division.

INSTRUCTIONS FOR USE

The unscored, thick-walled ampoules of this SRM must be opened with care and attention. Score the ampoule completely around the neck with a sharp triangular file or other scoring tool. Wrap the body of the ampoule in a thick cotton towel or use leather gloves while snapping the neck from the body of the ampoule.

Aliquots for analysis should be withdrawn at 20 °C to 25 °C and used immediately after opening the ampoules. Samples must be processed without delay for the certified values to be valid within the stated confidence intervals.

NOTICE AND WARNING TO USERS

Handling and Storage: Sealed ampoules, as received, should be stored in the dark at temperatures between 10 °C to 30 °C away from incompatible materials. Provide local exhaust or adequate ventilation in storage and laboratory facilities to meet published gasoline exposure limits. Prevent contact with heat, sparks, or open flame. Those handling gasoline should wear appropriate clothing and gloves to prevent skin contact with this material and appropriate safety goggles to prevent eye contact. Protect ampoules from physical damage. **Read the MSDS for this material before use.**

Preparation: This SRM was prepared by Spectrum Quality Standards, Inc. at their facilities in Houston, TX. All chemicals used in the preparation of this material were obtained from commercial sources. The synthetic gasoline base was prepared from twenty-one reagent-grade saturate, olefinic, and aromatic stock materials. A typical gas chromatogram of the reformulated gasoline base is shown in Figure 1. Three reagent-grade thionate stock materials were mixed with HPLC-grade ETBE. Known weights of synthetic gasoline base, thionate/ETBE mixture, and ETBE were combined, mixed, and chilled in a pressurized vessel. The solution was dispensed into 20-mL glass ampoules; the ampoules were cooled to -30 °C and flame sealed.

Table 1. Certified Weight Fractions for Selected Constituents of SRM 2296

Constituent	CAS Registry Number	Mass Fraction	95 % Analytical Confidence Interval
Total sulfur		40.0×10^{-6}	$39.6–40.4 \times 10^{-6}$
Benzene	71-43-2	1.0×10^{-2}	$1.00–1.02 \times 10^{-2}$
Toluene	108-88-3	8.02×10^{-2}	$7.92–8.11 \times 10^{-2}$
ETBE	637-92-3	13.02×10^{-2}	$12.87–13.17 \times 10^{-2}$

Table 2. Reference Values for Selected SRM 2296 Constituents

Constituent	CAS Registry Number	Mass Fraction ($\times 10^{-2}$)	95 % Analytical Confidence Interval ($\times 10^{-2}$)
1,2,4,5-Tetramethylbenzene	95-93-2	0.98	0.96 – 1.03
Naphthalene	91-20-3	1.17	1.15 – 1.19
Ethylbenzene	100-41-4	1.99	1.98 – 2.01
1,3,5-Trimethylbenzene	108-67-8	2.01	1.99 – 2.04
o-Xylene	95-47-6	2.01	1.99 – 2.05
1,2,4-Trimethylbenzene	95-63-6	2.05	2.02 – 2.08
m-Xylene and *p*-Xylene	108-38-3, 106-42-3	5.98	5.96 – 6.02
Total identified aromatics		25.38	25.27 – 25.56
1-Pentene	109-67-1	0.75	0.73 – 0.78
2,3-Dimethyl-2-butene	563-79-1	1.61	1.59 – 1.64
1-Heptene	592-76-7	1.63	1.60 – 1.66
Total identified olefins		4.14	4.12 – 4.18
n-Pentane	109-66-0	3.63	3.62 – 3.64
n-Hexane	110-54-3	3.77	3.76 – 3.78
n-Decane	124-18-5	4.21	4.20 – 4.22
n-Heptane	142-82-5	7.92	7.91 – 7.93
2,4-Dimethylpentane	108-08-7	8.05	8.04 – 8.06
n-Octane	111-65-9	8.13	8.12 – 8.14
Cyclohexane	110-82-7	9.01	9.00 – 9.02
2,2,4-Trimethylpentane	540-84-1	12.02	12.01 – 12.03
Total identified saturates		57.10	57.05 – 57.14
Thiophene	110-02-1	0.0031	0.0030 – 0.0032
benzo[*b*]thiophene	95-15-8	0.0036	0.0035 – 0.0037
3-Methylthiophene	616-44-4	0.0069	0.0068 – 0.0070
Water	07732-18-56	0.018	0.017 – 0.019
Total oxygen from identified organic oxygenates		2.06	2.01 – 2.08

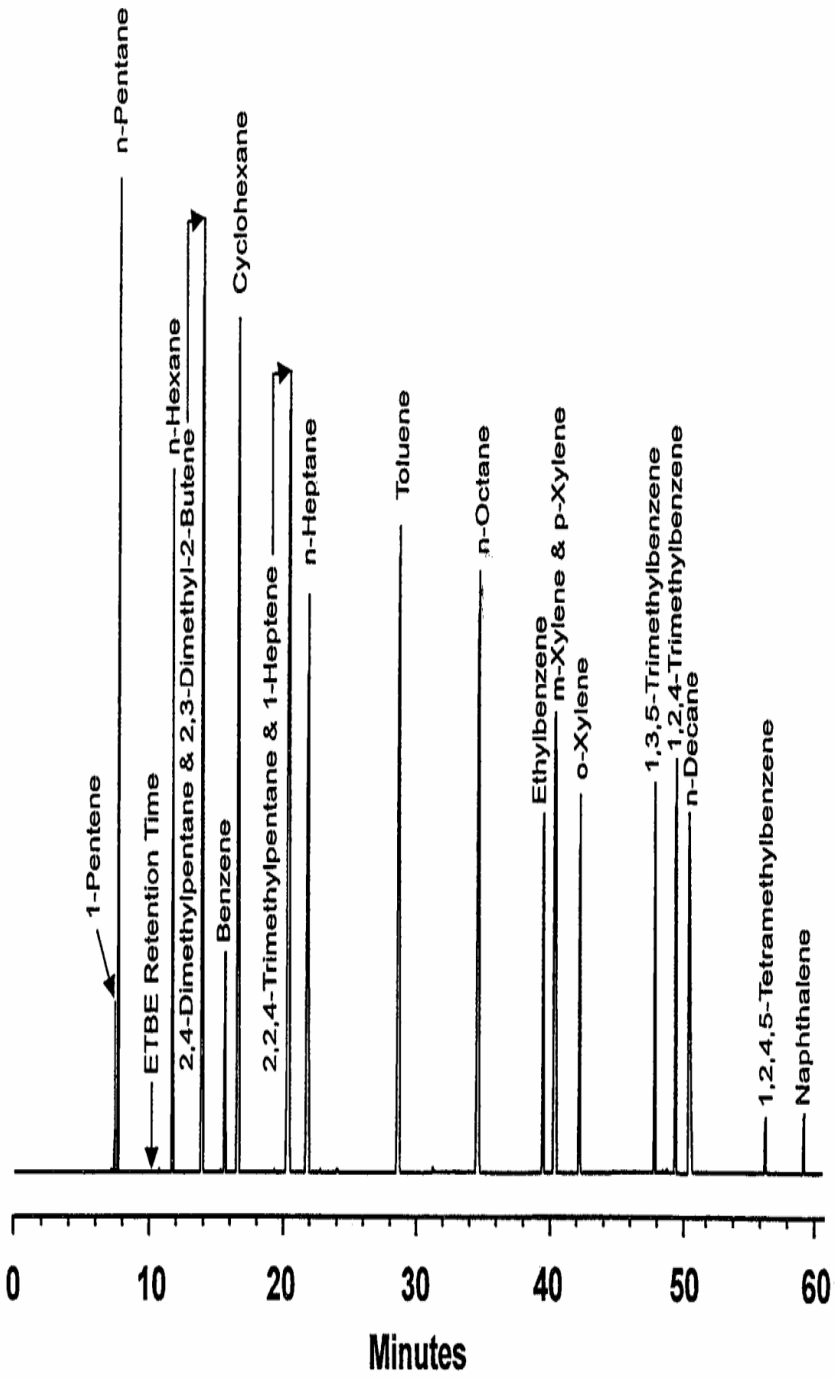

Figure 1. Chromatogram of reformulated gasoline base. Conditions: 100-m methylpolysiloxane column; injector temperature 200 °C; split ratio 200:1; initial temperature 35 °C, hold 10 min, programming rate 4 °C per min to 200 °C, final hold 10 min; detector temperature 280 °C. Except for *m*-xylene and *p*-xylene, the components unseparated by the conditions used to obtain the chromatogram in Figure 1 may be separated using the following: 30-m (6 % cyanopropyl) methylpolysiloxane column; injector temperature 200 °C; split ratio 200:1 initial temperature 30 °C, initial hold 5 min, programming rate 25 °C per min to 200 °C, final hold 0.2 min; detector temperature 280 °C.

REFERENCES

[1] Kelly, W.R.; Paulsen, P.J.; Murphy, K.E.; Vocke, R.D.; Chen., L.-T.; Anal. Chem. Vol. 66, p. 2505 (1994).

[2] ISO; *Guide to the Expression of Uncertainty in Measurement*; ISBN 92-67-10188-9, lst ed.; International Organization for Standardization: Geneva, Switzerland (1993); see also Taylor, B.N.; Kuyatt, C.E.; *Guidelines for Evaluating and Expressing the Uncertainty of NIST Measurement Results*; NIST Technical Note 1297; U.S. Government Printing Office: Washington, DC (1994); available at http://physics.nist.gov/Pubs/.

Certificate Revision History: 22 February 2006 (Editorial changes); 24 January 2006 (This revision reflects an editorial change); 30 December 2005 (This technical revision reports an extension of the certification period); 10 March 1998 (Original certificate date).

Users of this SRM should ensure that the certificate in their possession is current. This can be accomplished by contacting the SRM Program at: telephone (301) 975-6776; fax (301) 926-4751; e-mail srminfo@nist.gov; or via the Internet at http://www.nist.gov/srm.